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RECENT PROGRESS OF STUDY ON THE MOLECULAR THIN FILMS FOR ELECTRONICS

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Abstract In the broadest sense, molecular electronics covers the molecular materials and the use of these materials to fabricate into micro-devices which perform a signal processing or transformation function. Molecular thin films are important to molecular electronics because they are the basic component of making such devices. A brief review of our recent research works on molecular materials, physical properties of their thin films is outlined. In addition, light-emitting diodes and gas sensor are also included.

INTRODUCTION

Molecular thin films for electronics have attracted world-wide attention in recent years due to their significant academic senses and prospect in potential application. Molecular electronics is a new branch of science and technology.[1-2] It aims at creating new components for informatics and microelectronics based on organic conducting polymers, biopolymers, charge transfer salts, organometallic and other molecular materials. Molecular electronics has many advantages over the conventional solid-state electronics. However, to realize these ambitious projects there are many problems to be solved. Theory, materials and related technology are three main factors for the development of molecular electronics. The optical, electrical, chemical and thermodynamical properties of organic molecules together with their behavior of thin films should be carefully studied.

In this article, we will give a brief introduction to the molecular materials and their thin films, and then report progress in electronic devices. Results shown here are from our own laboratory.

DESIGN AND SYNTHESIS OF MOLECULAR MATERIALS

Molecular materials are composed of molecule component constructed by chemical bonding and through van der Waals interaction. To date, near ten million of organic compounds have been synthesized and they are still coming out at a rate of over hundred thousand per year. In so many organic solids, what physical and chemical properties are interesting and how do they offer opportunity for application? The reasons why the molecular materials are paid great attentions also comes mainly from two background besides to answer above scientific question: (1) after 40 year's development a flourishing present of solid state electronics comes into being which uses inorganic semiconductor crystals as its material base, however, further increasing the degree of integrity requires other ways. Scientists proposed a way to control the movement of electrons within an organic molecule, thus making the molecule aggregation a device with special function. This kind of device will probably become new one in 21th century. (2) Electronic properties, conducting mechanism and influence of the impurity in organic solid differ from that of traditional inorganic semiconductors. By studying the relationship between structure and property as well as its special physical property, it is possible to design molecules, condensed states and devices, and then to invent novel electronic materials with which current electronic materials are beyond compare. We focus our attentions on organic conductors[3] and superconductors,[4] organic nonlinear optical materials,[5] organic ferromagnetic compounds,[6-7] organic semiconductors[8] and newly discovery C_{60}.[9-10]

HIGH CONDUCTIVE LANGMUIR-BLODGETT (LB) FILMS

The requirements responsible for high conductivity in charge transfer (CT) salts are: (1) donor (D) and acceptor (A) are in separate stacks; (2) partial charge transfer (i.e., a mixed valence state); (3) equivalent intermolecular distance within each segregated stack. However, it is difficult to control the crystal structure artificially. Moreover, what happens in the LB system? We designed and synthesized amphiphilic donor and acceptor, i.e., 2-Octadecyl-7,7,8,8-tetracyanoquinodimethane (referred to as C_{18}TCNQ)

and 2,3-dimethylthio-6,7-dihaxadecylthiotetrathiafulvalene (known to C_1TTFC_{16}).[11] An alternative LB films in which the donors and acceptors are in separate stacks were constructed.

The $\sigma_{//}$ and $\sigma_{\perp}$ are the conductivities parallel and perpendicular to the LB films, respectively. The data clearly show as follows. (1) The ratios of $\sigma_{//}/\sigma_{\perp}$ are as high as 8-11 orders of magnitude, demonstrating very large anisotropy. (2) With iodine doping, the conductivities are increased by 2-4 orders of magnitude. (3) The most important feature is that the conductivities for alternating LB films are 2-5 orders of magnitude higher than that of mixed LB films. The donor molecules ($C_{18}TCNQ$) and acceptor molecules (C_1TTFC_{16}) took the form of segregated column in the alternating LB films. This is just the requirement for appearing high conductivity in CT crystalline. It indicates that this requirement is also suitable for the LB film system.

MAGNETIC PROPERTIES OF LB FILMS

To obtain organic ferromagnetic materials, one must make the organic molecules to have a net magnetic moment, and then make the magnetic moments to array orderly with ferromagnetic interactions. We synthesized a compound 2-[4-(hexadecyloxy) phenyl]-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-N-oxide (HTDIOO) with a long hydrophobic chain, suitable for LB film formation and a nitroxyl free radical, as reliable sources of magnetic moment.

A quasi-one-dimensional band structure composed of magnetic domains in the area of $25.7 \times 25.7\ \mu m^2$ of the LB films was found in the magnetic force microscopy (MFM) image.[12-13]

SECOND HARMONIC GENERATION IN LB FILMS OF AN ASYMMETRICAL PHTHALOCYANINE

Phthalocyanine, which is a π-conjugated macrocyclic molecule, usually shows third-harmonic generation. After chemical modification by attaching donor-acceptor substituents to its peripheral ring, intramolecular charge transfer through the π-conjugated

system is created. This makes phthalocyanine a second-harmonic generation (SHG) active molecule. The LB film technique offers a way to create non-centrosymmetric structure which in principle is a requirement for SHG materials. Here we report the LB film fabrication of an asymmetrically substituted phthalocyanine consisting of three *t*-butyl groups as donor substituents and one nitro group as an acceptor substituent, namely nitro-tri-*t*-butylphthalocyanine both in pristine form and in alternating form alternating either with tetra-*t*-butylphthalocyanine or arachidic acid. We demonstrate an alternative strategy for improving the SHG behavior in LB films.[14]

In contrast to our previous work,[15] these films exhibit nearly quadratic dependence of SH intensity on the film thickness up to nine bilayers. This result indicates alternating layers with AA or BuPc can avoid continuous degradation of alignment in the subsequent layer. Furthermore, the passive layers can also reduce the tendency of the molecules to invert during deposition and hence avoid the cancellation of the nonlinearilities between the successive layers.

LIGHT-EMITTING DIODES

There is a continuing interest in light emitting diodes (LEDs) due to the strong potential for application in displays and lighting. Although significant progress has been achieved in recent years, there are still a number of problems delaying their practical application. To increase the quantum efficiency in these devices, low work function metals like Ca and Mg must be used as a negative electrode. However, these metals are too active so that these devices have to operate in an inert atmosphere and in turn the stability of these devices is very limited. Moreover, photoluminescence efficiency can be increased in a polymer by separating the polymer chains and electroluminescence (EL) performance can be improved by the uniformity and the amorphous nature of poly(p-phenylenevinylene) (PPV).

LB technique used in LED fabrication may have a few advantages: (1) organized emitting layers; (2) thickness precisely controlled; (3) molecular thin emitting layer achievable; and (4) small operation voltage required.

Based on these consideration, we designed an alkoxyl cyano substituted derivative of PPV. The cyano groups increase the electron affinity of the polymer thereby improving the stability of EL devices by facilitating electron injection from stable electrode such as aluminum. The alkoxyl groups, on the one hand, satisfy the requirement for the LB technique by enhancing the solubility in common organic solvent; on the other hand, increase the van der Waals interaction force between the alkoxyl chains to form stable monolayer at the air-water interface. A third function is to enhance the efficiency by deducing the crystallinity of the polymer.

The I-V characteristics of an ITO/PPV/C16-CNPPV LB film/Al diode reveals good rectifying behavior. At forward bias higher than 5 V, uniform visible light emission can be clearly seen in a dark room.[16] The driving voltage of such LED fabricated with LB films is lower than that of spin casting film LEDs.

A NOVEL GAS SENSOR

There are numerous physical principles upon which sensor elements could be based. In the literature, mainly three kinds of sensor structures have been investigated. They are microelectrodes, quartz crystal microbalance (QCM) and surface acoustic wave (SAW) device. We demonstrate an optical Mach-Zhender interferometer as a novel sensor element incorporating with LB films of an amphiphilic metalloporphyrin, cobalt (II) 5,10,15-tri(*p*-octadecyloxyphenyl)-20-(*p*-hydroxyphenyl) porphyrin ($CoPPC_{18}$). The preliminary result indicates that the sensor is sensitive and reversible on exposure to NO_2 gas at room temperature.[17]

The possible mechanism of such a gas sensor is as follows. On exposure of the sensor element, a change in the refractive index occurs as a consequence of the interaction between the gas molecules and the active LB layers. This change influences the propagation behavior of the light in the waveguide, which leads to a phase shift in the sensing arms. Finally, the change in phase causes the output intensity of the Mach-Zehnder interferometer to vary in a manner which depends on the concentration of the gas and the exposure time of the device.

In summary, molecular materials will be bound to show incomparable advantages over inorganic electronic materials. The relationship between structure and property of molecular thin films and the mechanism of physical phenomenon must be further studied. In the exploration of their application, emphasis should be placed on the high-tech fields, and then to enhance the research on new generation of molecular devices.

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